

Interim Report

**SURFACTANT-ENHANCED SODIUM BICARBONATE FLOODING**

Project OE6

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## ABSTRACT

Three anionic and four nonionic surfactants were tested for their emulsification behavior with Tronacarb™ (sodium bicarbonate) and Wilmington crude oil. Three of the surfactants were found to enhance the solubilization of oil in the brine phase in the presence of Tronacarb according to the screening guide established in this study. Interfacial tension measurements were made on the most promising systems. The results support the hypothesis that a synergistic relationship can exist between low concentrations of synthetic surfactant and Tronacarb. In batch experiments using kaolinite and in a linear coreflood using consolidated Berea sandstone, Tronacarb reduced adsorption of surfactant by up to 93 percent. Tronacarb was less effective in preventing adsorption onto crushed Berea sandstone probably due to an unusually high amount of ferrodolomite (calcium magnesium carbonate with iron impurities).

The following conclusions have been made from the results of this work.

1. Addition of water-soluble synthetic surfactants to brines containing Tronacarb enhances the aqueous solubility of surfactants formed in situ.
2. The greatest solubilization of oil into the brine phase occurs when Tronacarb is used with synthetic surfactant.
3. The use of Tronacarb in combination with synthetic surfactants results in ultralow interfacial tension upon contact with the oil phase.
4. Tronacarb decreases the temperature at which nonionics can solubilize oil effectively (lower IFT). The use of nonionics at lower temperatures will reduce adsorption significantly.
5. Tronacarb is as useful as higher pH alkaline agents in preventing adsorption of anionic surfactants.

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## TERMINOLOGY USED IN THIS STUDY

Petroleum Surfactants - Surface active agents capable of reducing the interfacial tension between brine and oil.

Natural surfactants - Petroleum surfactants that are in acidic crude oils before having contact with alkaline solutions.

In situ generated surfactants - Petroleum surfactants that are generated by contacting an acidic crude oil with brines containing an alkaline chemical. These petroleum surfactants are also referred to as petroleum soaps.

Synthetic surfactants - Man-made surfactants. In this study, the synthetic surfactants are added to the alkaline chemical solution to enhance the overall performance of the in situ generated surfactants.

Creaming - Emulsification of oil and brine followed by separation into two emulsions. One emulsion generally has a greater amount of oil than the other. In some cases, a third emulsion will appear near the interface.

## INTRODUCTION

The objective of this research is to improve the oil displacement efficiency of the Tronacarb process\*\* by adding a low concentration of synthetic surfactant to the chemical formulation.

Previous investigations at NIPER have shown that low pH alkaline chemicals, such as sodium bicarbonate or mixtures of sodium carbonate and sodium bicarbonate, offer numerous advantages over the commonly used alkaline flooding agents (i.e., sodium hydroxide and silicates). Reduced mineral/alkali interactions, minimal loss of alkalinity, and reduced silicate scale formation are some of the advantages gained by using less harsh alkaline chemicals. Moreover, the weaker alkaline chemicals function in many of the same ways as the stronger alkaline agents. Oil displacement using the weaker alkaline chemicals can result from mechanisms other than lowering of interfacial tension. These mechanisms include: emulsification and coalescence, wettability alteration, and reduced interfacial shear viscosity between viscous crude oils and alkaline brines.<sup>1</sup>

The main problem associated with using low pH alkaline chemicals which has in the past deterred researchers from pursuing this process is that only a small fraction of the components in crude oils react to form surfactants. The use of weaker alkaline chemicals does not result in ultralow interfacial tension (high capillary number). Hence, only a small amount of the trapped residual oil is mobilized from the rock's pore spaces.

This report describes a process that uses both a weak alkaline chemical, sodium bicarbonate, and a low concentration of synthetic surfactant to improve the oil displacement efficiency of the Tronacarb process. The flooding pH of the Tronacarb process is  $8.8 \pm 0.3$ .

In chemical flooding, the interfacial tension between the oil and brine phase has the greatest effect on the amount of oil recovered. In surfactant flooding, low interfacial tension can easily be achieved. However, using surfactants alone is not cost effective due to the high concentration required to overcome adsorption losses. In addition, the oil recovery efficiency

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\*\* Alkaline flooding using Tronacarb, Kerr-McGee's brand of sodium bicarbonate.



obtained using surfactants is greatly affected by the salinity and temperature of the reservoir. The performance of a surfactant flood can suffer severely if the reservoir salinity is as little as 0.5 percent above or below the optimal region.

There are several advantages gained by combining alkaline chemicals with surfactants. Several researchers have found that by increasing the pH of the reservoir brine there is a significant improvement in the cost and oil recovery efficiency when compared with chemical flooding using surfactants and/or polymers alone.<sup>2-5</sup> In fact, at low concentrations most alkaline chemicals are compatible with surfactants and appear to enhance the performance of the chemical formulation.<sup>2</sup> Alkaline chemicals can have a dramatic effect on the ionic environment, they can raise or lower the optimal salinity of synthetic surfactants, and extend their optimal region. Alkaline chemicals can decrease emulsion stability by preventing the formation of rigid interfacial films,<sup>6</sup> alter rock wettability,<sup>5</sup> and modify mineral surfaces leading to reduced adsorption of the more expensive chemical components.<sup>2</sup>

In this interim report, the interaction of Tronacarb with three anionics and four nonionic surfactants is discussed. The results of two surfactant adsorption experiments using kaolinite (clay) and crushed Berea sandstone are reported. In addition, this report contains the results from a linear coreflood experiment designed to determine the effectiveness of a Tronacarb preflush in reducing surfactant adsorption. A brief summary of the tasks performed and reported herein is presented below. These tasks are in accordance with the OE6 cooperative proposal NIPER No. 85-132B.

### **Task 1 - Phase Behavior**

Identify the optimal salinity for various surfactants and Wilmington crude oil using sodium chloride alone and using sodium chloride plus Tronacarb (sodium bicarbonate).

## Task 2 - Interfacial Tension (IFT)

Measure the IFT on the most promising systems found in task 1. Compare the results of brine solutions containing preformed surfactant and Tronacarb, surfactant alone, and Tronacarb alone.

## Task 5 - Static Adsorption Experiments

Measure surfactant adsorption onto kaolinite and crushed Berea sandstone in separate batch experiments at 23° and 70° C. Analyze the effluent surfactant concentration to determine the extent of surfactant adsorption from brines containing either sodium chloride alone or sodium chloride plus Tronacarb.

## EXPERIMENTAL

The optimal salinities of various anionic and nonionic surfactant solutions were evaluated by performing salinity scan experiments at a water/oil ratio of 1 using Wilmington crude oil (acid number 2.1 mg of KOH/g sample). The salinities tested ranged from 0.5 to 20 percent NaCl. At least six different salinities were tried for each surfactant/brine mixture. The brines contained added synthetic surfactant and either NaCl alone or NaCl plus NaHCO<sub>3</sub> (Tronacarb). Due to the low total concentration of surfactant in most of these systems, optimal salinity was not completely identified by emulsion phase behavior alone. A range of optimal salinities was determined for each system according to the screening guide presented in table 1. Optimal salinity was further identified using the interfacial tensiometer.

Interfacial tension measurements were performed using a spinning drop interfacial tensiometer. IFT measurements were made at the same temperature that the salinity scan experiments were performed except when the effect of temperature was studied. Equilibration of the two phases occurred while spinning. IFT measurements were obtained immediately after the oil contacted the brine phase and continued up to 6 hours or until the change in the IFT was less than 0.15 percent/minute.

Batch experiments were performed using kaolinite (clay) at a solid/liquid ratio of 0.1 and crushed Berea sandstone at a solid/liquid ratio of 1.0. Brines initially contained approximately 4 millimoles/liter of an alcohol

ethoxysulfate (Neodol® 25-3S), and either 3 percent NaCl or 1.5 percent NaCl plus 2.16 percent NaHCO<sub>3</sub> (Tronacarb). The minerals and brines were sealed in 250 mL Teflon bottles and shaken continuously at room temperature (23° C) and in a water bath (70° C). Aliquots were removed periodically and centrifuged for 1 hour at 2,000 rpm to remove fine particles. Sulfate content of the samples was analyzed by colorimetric titration using a standardized Hyamine 1622® titrant.

Two linear corefloods were performed at 49° C using unfired consolidated Berea sandstone. Prior to surfactant injection, the two Berea cores were equilibrated with a 3 percent NaCl solution containing 0.1 percent each of calcium and magnesium ions. The two Berea cores were then injected with either 3 percent NaCl brine or 1.5 percent NaCl + 2.16 percent NaHCO<sub>3</sub> (Tronacarb) brine. After injecting 2 pore volumes of each preflush solution, the cores were continuously injected with approximately 0.15 percent of a synthetic surfactant (Neodol ethoxysulfate). Surfactant adsorption values were determined by the difference between the integrated areas of the injected and recovered surfactant effluent profiles.

## RESULTS

### Emulsion Screening Tests

Table 1 lists the seven surfactants tested for their phase behavior with Tronacarb, the test temperature, synthetic surfactant concentration, and some of the physical properties of the surfactants.

In this study, the in situ generated surfactants are formed by the chemical reaction between the alkaline chemical and the organic acids present in the Wilmington crude oil. The synthetic surfactant is added directly to the brine solution. The anionic surfactants chosen for this study were all water soluble. Two of the nonionics were water soluble and two were oil soluble. Since the in situ generated surfactants are very lipophilic,<sup>3</sup> part of the screening procedure was to determine if the in situ generated surfactants became more water-soluble in the brine in the presence of the synthetic surfactant. The appearance of an amber color brine is indication that the alkaline agent is reacting with the crude oil and that the in situ generated surfactant is partially water soluble in the presence of the synthetic surfactant.

Of the seven surfactants tested in this study, Neodol 25-3S (photograph 1), TRS-10-410 (photograph 2) and Neodol 45-13 (photograph 3) were found to enhance the solubility of the in situ generated surfactants in the brine phase. Brines containing Neodol 25-3S and TRS-10-410 alone showed a small but detectable amount of natural surfactant (photographs 4 and 5 respectively). In general, these natural surfactants are partially ionized organic acids that become highly ionized and surface active at higher pH. When mixed with a water-soluble synthetic surfactant, these natural surfactants became partially water soluble. There was no indication that the in situ generated surfactants were even slightly water soluble when using Tronacarb alone.

After emulsification and phase separation (creaming), brines containing Tronacarb and synthetic surfactant were determined to be compatible if they showed enhanced miscibility of the oil in the brine phase. In some systems, the optimal salinity region was determined by the appearance of a greenish/grey middle layer. Other systems were found to be optimal if they exhibited a light tan emulsion during emulsification (conforming with Shell's alkaline/surfactant screening guide).

Photograph 6 shows the phase behavior results obtained using Tronacarb with Neodol ethoxysulfate. The photograph shows that emulsification of the lower phase increases with increasing salinity up to the optimal salinity region where there is the appearance of a pseudo-third phase. The salinity at which this third phase forms is the point where the surfactants partition between the oil and brine phase. At 10.8 percent sodium chloride (11.4 percent based on total sodium content) an over-optimum condition results characterized by the salting out of the petroleum soaps which results in the appearance of a clear lower phase.

For comparison, photograph 7 shows the phase behavior for the system using Neodol ethoxysulfate alone with sodium chloride. The optimal salinity for this system is less apparent probably due to the lower total surfactant concentration in this system. The onset of lower phase emulsification occurs at 15 percent sodium chloride whereas over-optimum conditions occur at approximately 20 percent.

Photographs 8 and 9 show the phase behavior using the nonionic Neodol 45-13 in brines containing Tronacarb or plain brine, respectively. Again, in the presence of the synthetic surfactant, there is a distinguishable

difference in lower phase emulsification when Tronacarb is present. The absence of an amber color brine when Tronacarb is not present supports the hypothesis that sodium bicarbonate does react with the acidic components in Wilmington crude oil to form in situ generated surfactants. These in situ generated surfactants become significantly more water soluble when certain water soluble synthetic surfactants are added to the brine phase.

Table 1 summarizes the results from screening commercial surfactants for their compatibility with Tronacarb and Wilmington crude oil. The approximate optimal salinity range for those systems found compatible are also listed. Addition of Tronacarb to TRS-10-410 had a small influence on the phase behavior of this surfactant. The optimal salinity was found to be 1.8 percent with Tronacarb and 1.7 percent without Tronacarb. However, Tronacarb had a much greater effect on the ethoxylated surfactants. The use of Tronacarb with Neodol ethoxysulfate lowered the optimal salinity region of the surfactant from between 16 to 20 percent to between 8 to 11 percent. This concentration range is closer to the salinity of most oilfield reservoirs.

### Interfacial Tension

Supporting interfacial tension measurements were made on the most promising systems found in the emulsion screening tests. In most cases, IFT values less than 0.1 dyne/cm are necessary to start mobilizing crude oil from the capillary pore spaces and channels of the reservoir rock. Values less than 0.001 dyne/cm are needed to displace the crude oil effectively.<sup>4</sup> Interfacial tension measurements can help to quantify and rank each system in order of their potential ability to mobilize trapped oil.

### **Mixing In Situ Generated Surfactants With Anionic Synthetic Surfactants**

The interfacial tensions for brines containing Neodol ethoxysulfate and Tronacarb, at two salinities are shown in figures 1 and 2. The IFT of brines containing synthetic surfactant and sodium chloride at equivalent concentrations are also shown. Upon initial contact with oil, the systems that contained Tronacarb had very low interfacial tension (approximately 0.008 dyne/cm). This is caused by a high local concentration of surfactant near the oil/brine interface when the alkaline chemicals react with the acidic

components in the crude oil.<sup>8</sup> Upon aging, some of the surfactants diffuse into the oil phase, some diffuse into the brine phase, and some remain at the interface. The long-term IFT value reflects the amount of surfactant which remains interfacially active. At both salinities the equilibrated IFT for the Tronacarb systems were lower than for the chloride systems alone indicating that a higher concentration of surfactant remained interfacially active. The IFT results for Tronacarb plus sodium chloride alone against Wilmington crude oil ranged from 5 to 10 dyne/cm.

The interfacial tension for the Tronacarb/surfactant systems was also measured at 50° C to show that the transient behavior in IFT was not a result of bicarbonate decomposition at 70° C. Except for the increased rate of equilibration at the higher temperature, the results are similar indicating that chemical decomposition was not a problem.

Figure 3 summarizes the effect of adding sodium chloride to Tronacarb and Neodol ethoxysulfate. The data show that as salinity increases, the equilibrated interfacial tension decreases. This effect is shown at both 50° and 70° C. Surprisingly, at high salt concentrations, the IFT does not begin to increase as the petroleum soaps are salted out of solution. One explanation is that Neodol ethoxysulfate is still interfacially active at higher salinities. Another explanation is that the surfactants (in situ generated plus synthetic) are less water soluble at higher salinities. Therefore, they remain at the interface longer and are less likely to diffuse into the bulk aqueous phase. This would explain why the interfacial tension remained low at high salinities. The benefit of using the two chemicals together is that Tronacarb broadens the useful salinity region of Neodol ethoxysulfate to include lower salinity reservoirs. In addition, Tronacarb induces very low interfacial tension upon initial contact with Wilmington crude oil.

The IFT versus time for systems containing TRS-10-410 and Tronacarb at various salinities are shown in figure 4. The optimal salinity found in these measurements was equivalent to 1.8 percent sodium chloride which provided both a low equilibrium and minimum IFT value. This same salinity was found optimal in the emulsion screening tests because it had exhibited the longest lasting light tan emulsion. At lower salinities, IFT was favorable but the oil drop tended to adhere to the IFT glass capillary tube. At higher salinities, the

equilibrium interfacial tension increased and the time necessary to reach the IFT minimum value decreased.

Figure 5 compares the interfacial tension data obtained with brines containing Witco TRS-10-410 with either Tronacarb and sodium chloride or sodium chloride alone. The data show that ultralow IFT (less than .01 dyne/cm) occurs extremely fast in the system containing Tronacarb, whereas it takes approximately 80 minutes for the sodium chloride system to approach the same IFT.

### **Mixing In Situ Generated Surfactants With Synthetic Nonionic Surfactants**

The solubilization of oil using nonionic surfactants is greatly affected by temperature. Their performance markedly improves near the surfactant's cloud point temperature.<sup>9</sup> Cloud point is defined as that temperature at which a nonionic surfactant solution separates into surfactant-rich and brine-rich phases. Valaulikar and Manohar have associated this phenomena with the growth of micellar aggregates.<sup>10</sup>

Figure 6 shows the IFT results for brines containing 0.1 percent alcohol ethoxylate plus either Tronacarb plus sodium chloride or sodium chloride alone. In both systems, the highest salinities resulted in the lowest IFT at 75° C. Table 3 gives the cloud point of the four systems used in these measurements. At 5 equivalent percent sodium chloride, the cloud point for both the Tronacarb and chloride systems are closer to the IFT test temperature than for the 3 percent brine solutions. The improved solubilization of oil (low IFT) using 5 percent brines resulted from the test temperature being within 5° C of the cloud point.

There are problems associated with using nonionics near their cloud point. Verkruyse and Salter<sup>11</sup> found that adsorption of nonionic surfactants is dependent upon both the test temperature and the cloud point of the surfactant solution. Adsorption was found to be extremely high near the cloud point temperature. This implies that nonionics should be used at temperatures below their cloud point to minimize adsorptive losses.

Figure 7 indicates that by using the nonionic surfactant with Tronacarb, lower temperatures can be used to minimize adsorption losses while maintaining

a reasonable IFT. This shows that a synergistic relationship exists whereby the nonionic surfactant lowers the interfacial tension for the Tronacarb process and that Tronacarb reduces the temperature dependence for the nonionic surfactant.

## Surfactant Adsorption

### Batch Experiments

One of the most appealing features of the surfactant-enhanced Tronacarb process is how little synthetic surfactant is needed to affect large improvements in oil recovery at low chemical cost. The effective use of low surfactant concentrations is made possible due to the high pH of alkaline chemicals. At pH 9, rock surfaces are more negatively charged than at neutral pH. This helps to diminish adsorption of the negatively charged (anionic) surfactants thereby facilitating the use of low surfactant concentrations.

To quantify how much Tronacarb reduces surfactant adsorption, batch experiments were performed using Neodol ethoxysulfate. The minerals used were kaolinite (clay), a typical reservoir clay, and crushed Berea sandstone. The mineralogical analysis of the Berea sandstone used appears in table 3.

Figure 8 shows the adsorption kinetics of surfactant onto kaolinite at pH 6.6 and at pH 9. Tronacarb was found to be very effective in inhibiting surfactant adsorption onto kaolinite. Adsorption was reduced by 74 percent at 23° C and by 93 percent at 70° C.

Figure 9 shows the adsorption of surfactant onto crushed Berea sandstone. Tronacarb decreased adsorption by 7 percent at 23° C and by 17 percent at 70° C. In this case, the effectiveness of Tronacarb in preventing surfactant adsorption was less impressive. One possible explanation results from the unusually high amount of ferrodolomite found in the Berea sandstone. Ferrodolomite,  $\text{Fe}_x\text{Mg}_y\text{Ca}_x(\text{CO}_3)_n$ , may be dissolving into the solution introducing a constant supply of divalent ions. The divalent ions can cause bicarbonate precipitation or they can bind to minerals giving rise to a positively charged surface. The smaller effect of Tronacarb in inhibiting surfactant adsorption may be a result of bicarbonate loss or high divalent ions.



## Coreflooding

The effectiveness of Tronacarb in inhibiting surfactants adsorption was also evaluated by performing corefloods to compare the performance of Tronacarb and sodium chloride as preflush chemicals.

Figure 10 indicates that when preflushing with Tronacarb, the concentration of surfactant in the effluent reaches the injected concentration approximately 0.5 pore volumes sooner than when preflushing with sodium chloride. This demonstrates that Tronacarb can be used effectively to reduce surfactant adsorption on reservoir rocks.

Table 4 summarizes all the results by listing the surfactant adsorption in milliequivalents per 100 grams of rock. In the batch experiments, Tronacarb reduced adsorption onto kaolinite by 74 percent at 23° C and by 93 percent at 70° C. In the linear coreflood experiment, Tronacarb reduced surfactant adsorption by 74 percent at 49° C. These results are in good agreement with those obtained by Nelson et al.<sup>3</sup>, using sodium hydroxide and sodium metasilicate.

## DISCUSSION

These findings suggest that a synergistic relationship exists between Tronacarb, synthetic surfactant and Wilmington crude oil. Interfacial tension measurements obtained on those systems identified as compatible in the emulsion screening tests showed that Tronacarb enhanced the performance of these surfactants in several ways. First, the optimal salinity region of Neodol ethoxysulfate was broadened substantially to encompass a wider range of reservoir salinities. Second, addition of Tronacarb to nonionics reduced the temperature requirement needed for oil solubilization. Lastly, for all surfactants tested with Tronacarb, ultralow interfacial tension occurred upon initial contact with Wilmington crude oil. In oil recovery processes, the chemical slug propagates through a partially oil-saturated reservoir continually contacting fresh oil. A surfactant-enhanced Tronacarb solution will produce emulsions with this oil faster than either chemical component alone because of the rapid decrease in interfacial tension. The addition of surfactant to Tronacarb should result in a significant improvement in oil mobilization (higher oil recovery efficiency) when compared with using either surfactant or Tronacarb alone.

The use of nonionic surfactants has been of interest for a long time. The motivation for using nonionic surfactants is their insensitivity to high salinities and to divalent ions, by which they remain soluble and have less tendency to precipitate than sulfonates.<sup>12</sup> Prior research using nonionic surfactants has been discouraging due to unacceptably high adsorption of these surfactants. Our research using sodium bicarbonate indicates that nonionics can be used effectively in EOR if the pH of the reservoir is raised above neutral pH. This combination will reduce adsorption and lower the temperature at which the nonionic surfactant can solubilize oil efficiently (lower IFT).

The use of low surfactant concentrations in EOR would not be possible without the presence of a sacrificial adsorbate. In this study, we have found that Tronacarb is highly effective for use in protecting surfactants from excessive adsorption. In the batch experiment using kaolinite and in the linear coreflood using Berea sandstone, Tronacarb reduced surfactant adsorption by as much as 93 percent. By determining the extent of surfactant adsorption onto Berea sandstone, kaolinite, and other minerals, a chemical slug can be designed with the minimum surfactant concentration necessary to remain effective.

### EXPERIMENTAL CONCLUSIONS

1. In the emulsion screening tests, addition of synthetic surfactants to brines containing Tronacarb enhances the solubility of in situ generated surfactants into the aqueous phase.
2. The greatest solubilization of oil into the brine phase occurs when Tronacarb is combined with synthetic surfactants.
3. In all cases, the use of Tronacarb with synthetic surfactants results in ultralow interfacial tensions upon initial contact with the oil phase. This does not occur using synthetic surfactants alone or using Tronacarb alone.
4. Tronacarb reduces the temperature dependence for the synthetic nonionic surfactant (Neodol 45-13). The use of nonionics at lower temperatures will result in lowering of the interfacial tension and a reduction in adsorption of surfactant onto reservoir rock.

5. Tronacarb is as useful as higher pH alkaline agents in reducing adsorption of anionic surfactants.

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TABLE 1. - Commercial surfactants tested for their emulsion phase behavior with sodium bicarbonate (Tronacarb<sup>™</sup>).<sup>1</sup>

| Surfactants,<br>% active used    | Molecular<br>Weight<br>g/mole | Hydrophilic<br>Lipophilic<br>balance | Test<br>Temperature<br>° C | Approximate optimal<br>salinity region,<br>equiv. % w/v |                     |
|----------------------------------|-------------------------------|--------------------------------------|----------------------------|---|---------------------|
|                                  |                               |                                      |                            | NaCl<br>alone   | Tronacarb +<br>NaCl |
| <u>Petroleum sulfonates</u>      |                               |                                      |                            |   |                     |
| Witco TRS-10-40, 3%              | 330/350                       |                                      | 45                         | not compatible  |                     |
| Witco TRS-10-410, 1%             | 405/420                       |                                      | 45                         | 1.7 - 1.9   | 1.8 - 2.0           |
| <u>Alcohol Ethoxysulfate</u>     |                               |                                      |                            |   |                     |
| Neodol <sup>2</sup> 25-3S, 0.1%  | 439                           |                                      | 70                         | >16   | >9                  |
| <u>Nonionic Ethoxylates</u>      |                               |                                      |                            |   |                     |
| Neodol <sup>2</sup> 45-13, 0.1%  | 790                           | 14.4                                 | 70                         | not determined  | 5 - 6               |
| Neodol <sup>2</sup> 91-2.5, 0.1% | 279                           | 8.6                                  | 45                         | not compatible  |                     |
| Neodol <sup>2</sup> 25-3, 0.1%   | 336                           | 7.9                                  | 45                         | not compatible  |                     |
| Neodol <sup>2</sup> 91-6, 0.1%   | 425                           | 12.5                                 | 45                         | not compatible  |                     |

<sup>1</sup> Screening guide: Compatibility is determined by performing salinity scans using a broad range of salinities and narrowing it near optimal conditions. Before creaming, an amber-brown discoloration near the oil-water interface occurred in systems found compatible. This is due to an increased solubility of the in situ generated surfactants into the brine phase. After creaming, compatibility is indicated by a detectable increase in lower phase emulsification with increasing salinity.

<sup>2</sup> Product of Shell Chemical Company.

TABLE 2. - Cloud point of brines containing 0.1% Neodol 45-13 ethoxylate and either sodium bicarbonate (Tronacarb) plus sodium chloride or sodium chloride alone.

| Brines                                    | Cloud point, ° C |
|---|------------------|
| 1.2% NaHCO <sub>3</sub> (Tronacarb) plus: |                  |
| 4.2% NaCl                                 | 79.0             |
| 2.2% NaCl                                 | 87.5             |
| NaCl alone:                               |                  |
| 5.0%                                      | 81.0             |
| 3.0%                                      | 88.5             |

TABLE 3. - Mineral content of crushed Berea sandstone by X-ray diffraction, percent w/w.

| Quartz | Feldspar | Calcite          | Ferro-Dolomite | Siderite         | Kaolinite | Illite           | Mixed-Layer Illite/Smectite |
|--------|----------|------------------|----------------|------------------|-----------|------------------|-----------------------------|
| 88     | 3        | trc <sup>1</sup> | 4              | trc <sup>1</sup> | 5         | trc <sup>1</sup> | trc <sup>1</sup>            |

<sup>1</sup> - Less than 1%.

TABLE 4. - The effect of Tronacarb in reducing surfactant adsorption on various minerals.

| Rock   | milliequivalents adsorbed/100g rock |         |                                   |         |
|--|-------------------------------------|---------|-----------------------------------|---------|
|  | Chloride Brine<br>(23° C)           | (70° C) | Tronacarb Brine<br>(23° C)        | (70° C) |
| <u>Batch Experiments</u>                         |                                     |         |                                   |         |
| kaolinite<br>solid/liquid = 0.1                  | 1.36                                | 1.33    | 0.36                              | 0.09    |
| crushed Berea<br>sandstone<br>solid/liquid = 1.0 | 0.15                                | 0.12    | 0.14                              | 0.10    |
|  | Chloride Brine<br><u>(49° C)</u>    |         | Tronacarb Brine<br><u>(49° C)</u> |         |
| <u>Coreflood Experiment</u>                      |                                     |         |                                   |         |
| consolidated Berea<br>sandstone                  | 0.019                               |         | 0.005                             |         |

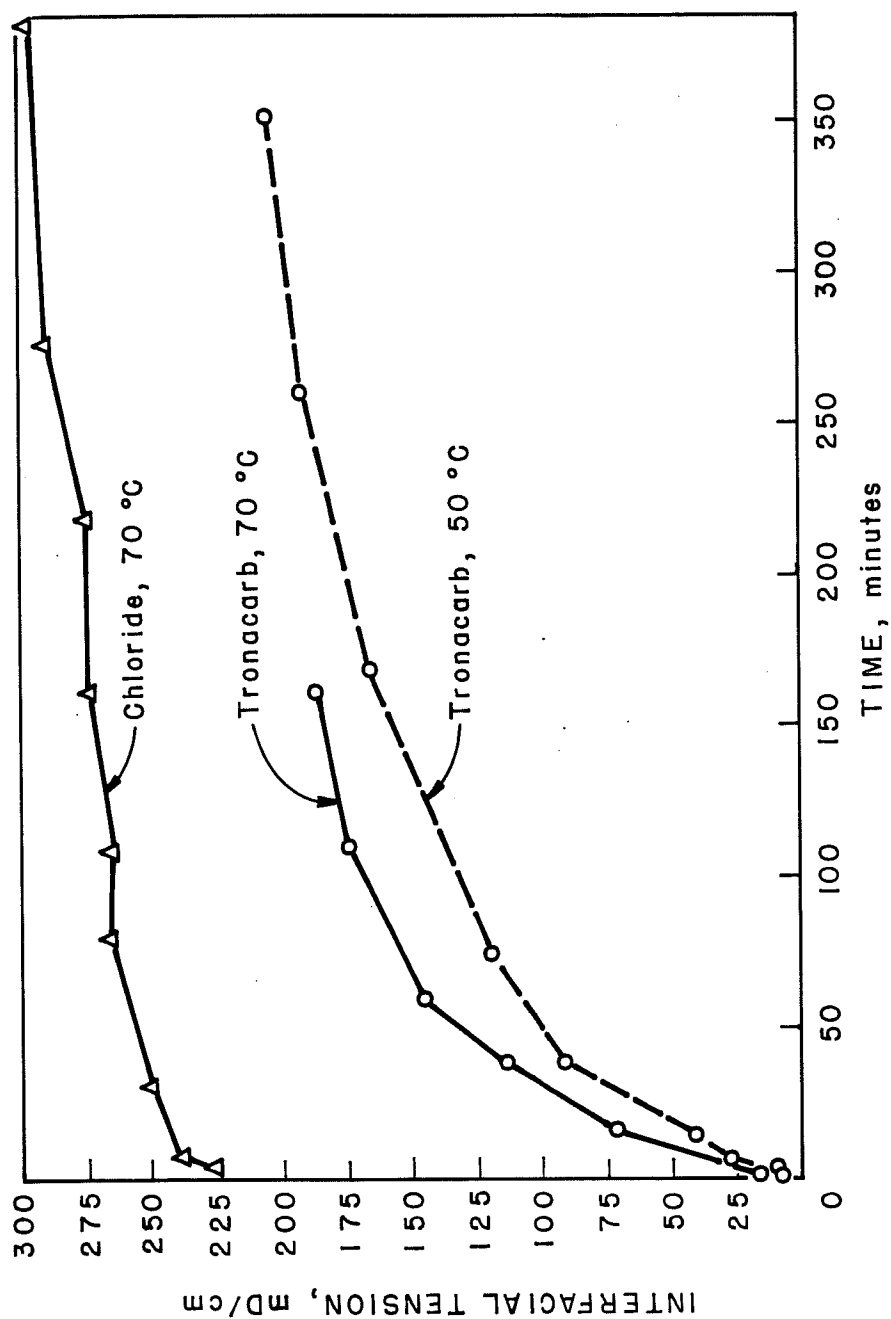


FIGURE 1. - Interfacial tension versus time for non-preequilibrated systems. Brines contain 0.1 percent Neodol ethoxysulfate and either 1.2 percent sodium bicarbonate plus sodium chloride or sodium chloride alone. The equivalent sodium chloride concentration is 9.66 percent based on total sodium.



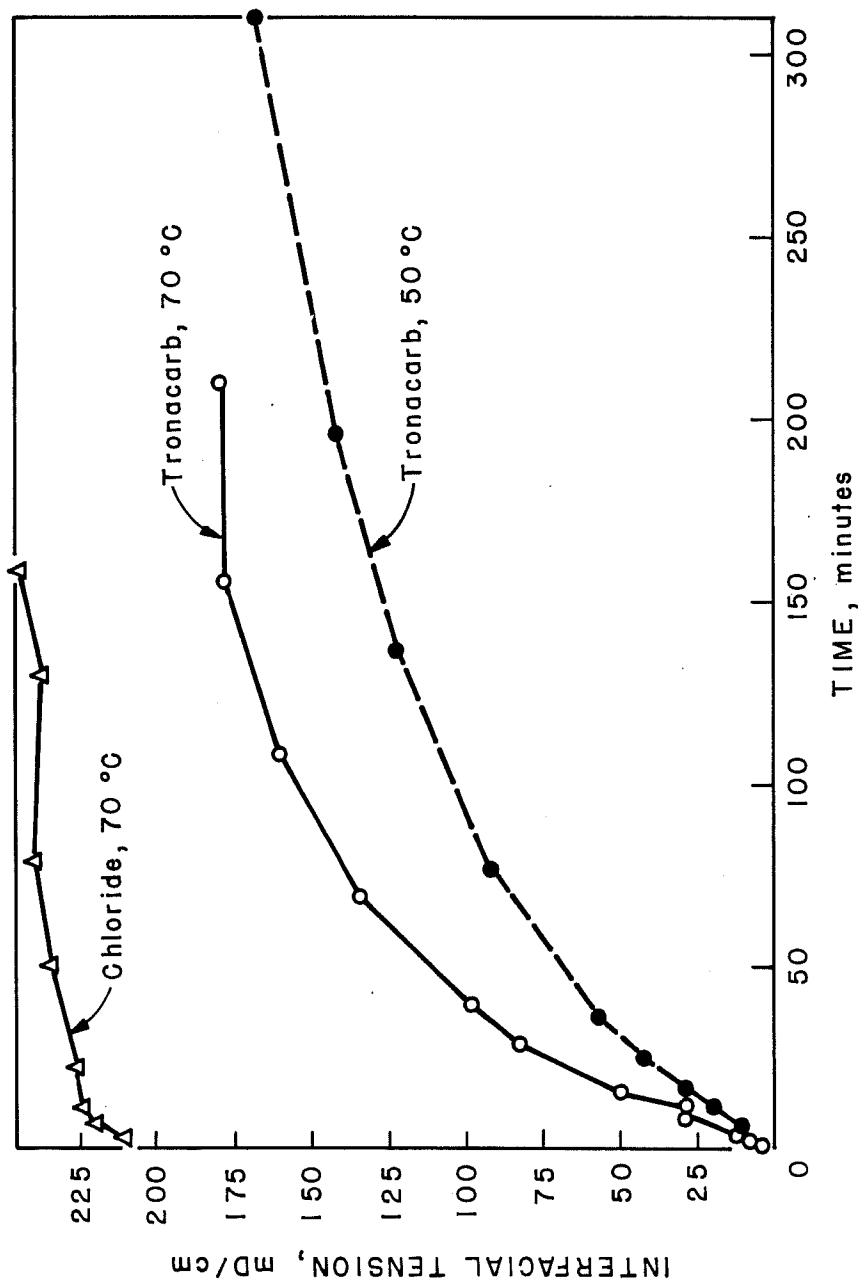


FIGURE 2. - Interfacial tension versus time for non-preequilibrated systems. Brines contain 0.1 percent Neodol ethoxysulfate and either 1.2 percent sodium bicarbonate plus sodium chloride or sodium chloride alone. The equivalent sodium chloride concentration is 10.66 percent based on total sodium content.

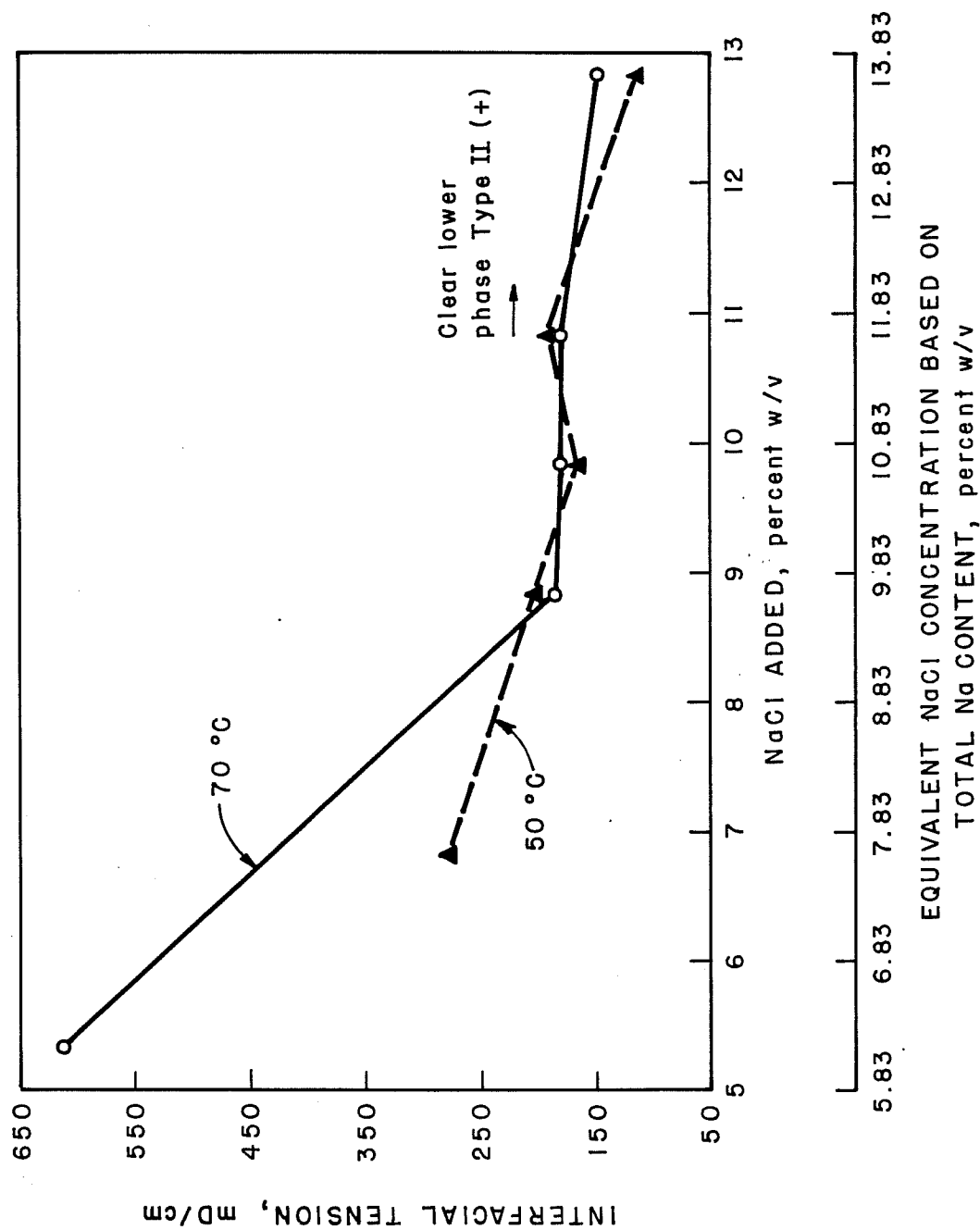


FIGURE 3. - Interfacial tension versus equivalent sodium chloride concentration for equilibrated systems containing 0.1 percent ethoxysulfate and either 1.2 percent sodium bicarbonate (Tronacarb) plus sodium chloride or sodium chloride alone. The oil used was Ranger zone Wilmington crude oil.

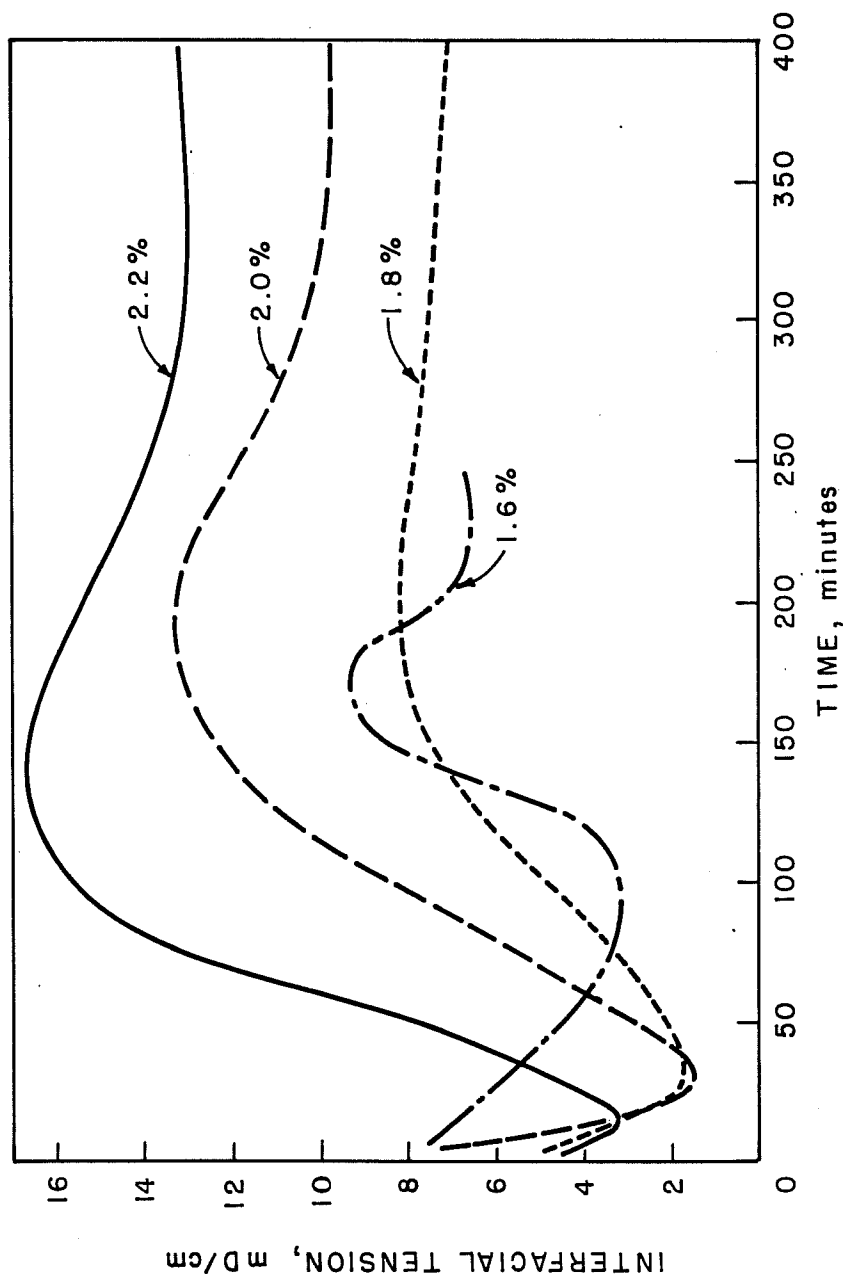


FIGURE 4. - Interfacial tension versus time for non-preequilibrated systems. Brines contain 1.2 percent sodium bicarbonate plus 0.1 percent active TRS-10-410. The equivalent sodium chloride concentrations shown are based upon the total sodium in the brine phase. The oil used was Ranger zone Wilmington crude oil. The IFT test temperature was 45° C.

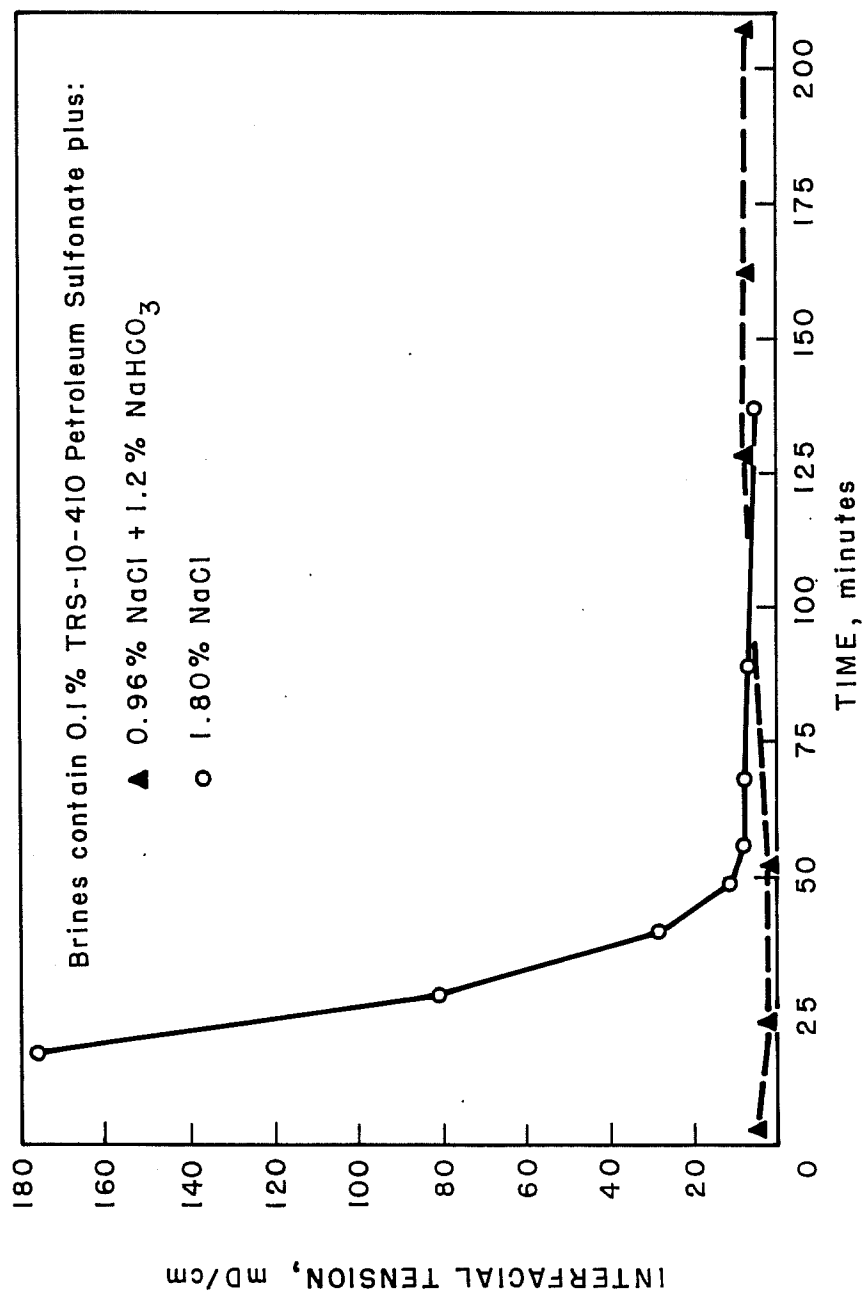


FIGURE 5. - Interfacial tension versus time for non-preequilibrated systems. The oil used was Ranger zone Wilmington crude. The IFT test temperature was 45° C.

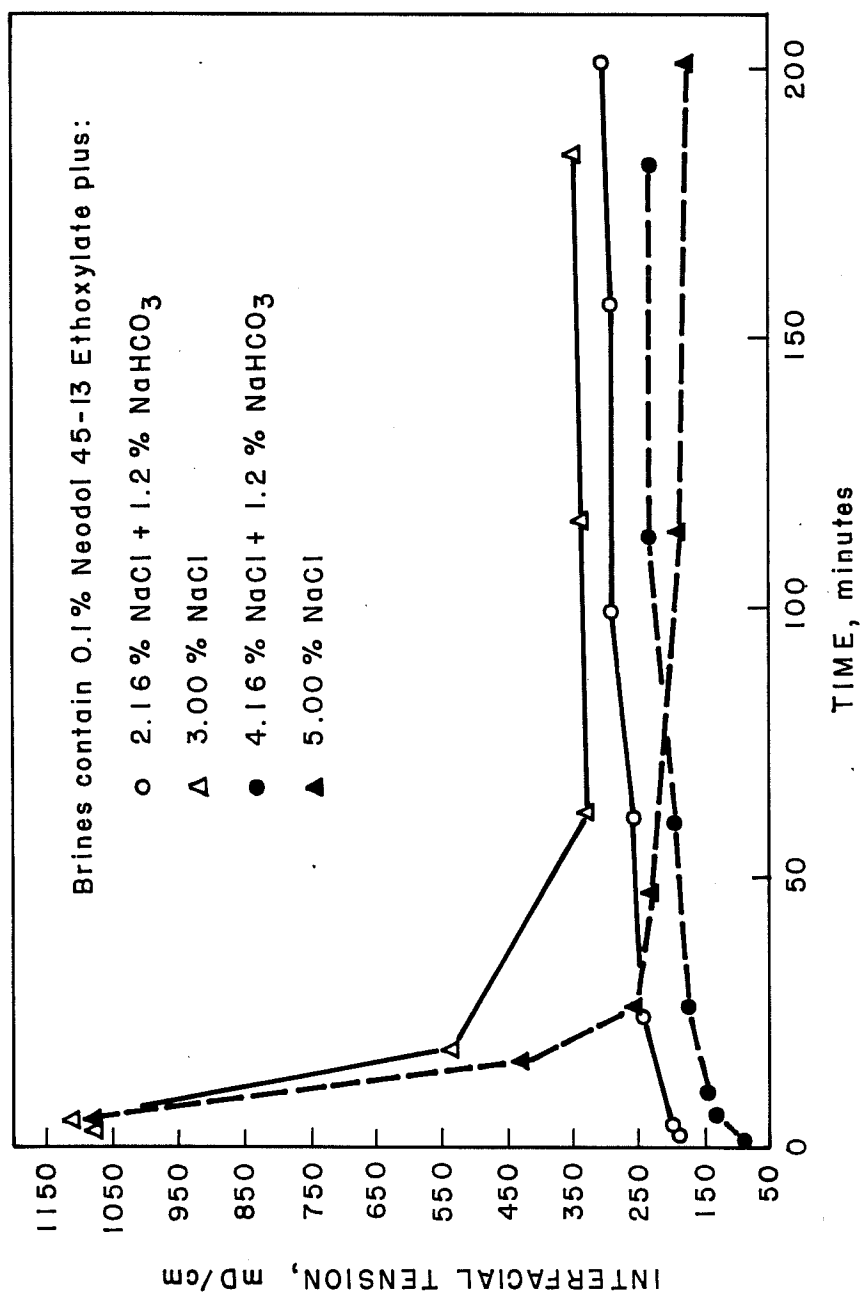


FIGURE 6. - Interfacial tension versus time for non-preequilibrated systems containing nonionic surfactant and Ranger zone Wilmington crude oil. The IFT test temperature was 75° C.

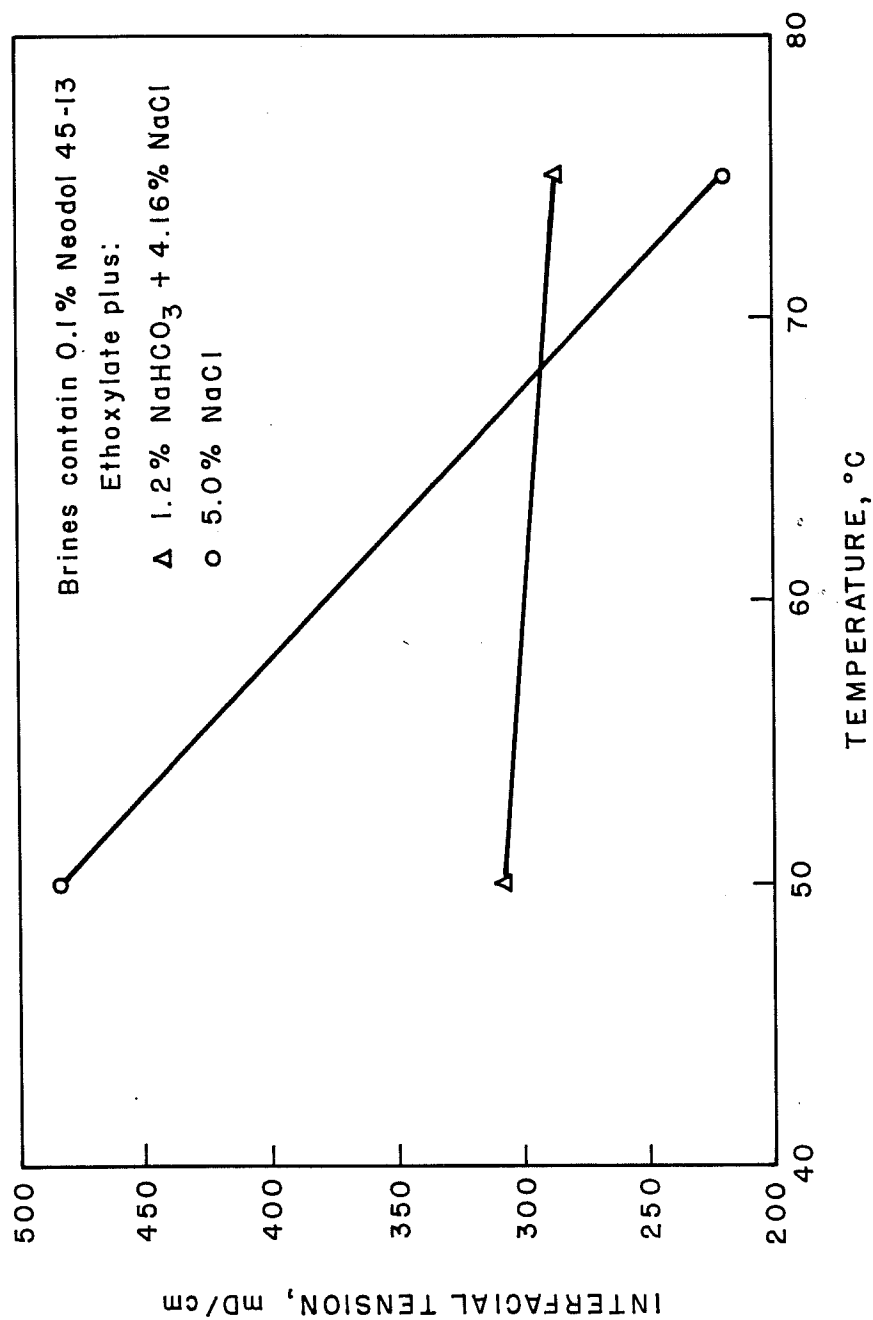


FIGURE 7. - Interfacial tension as a function of temperature for equilibrated systems containing nonionic surfactant and either Tronacarb plus sodium chloride or sodium chloride alone. The oil used was Ranger zone Wilmington crude oil.

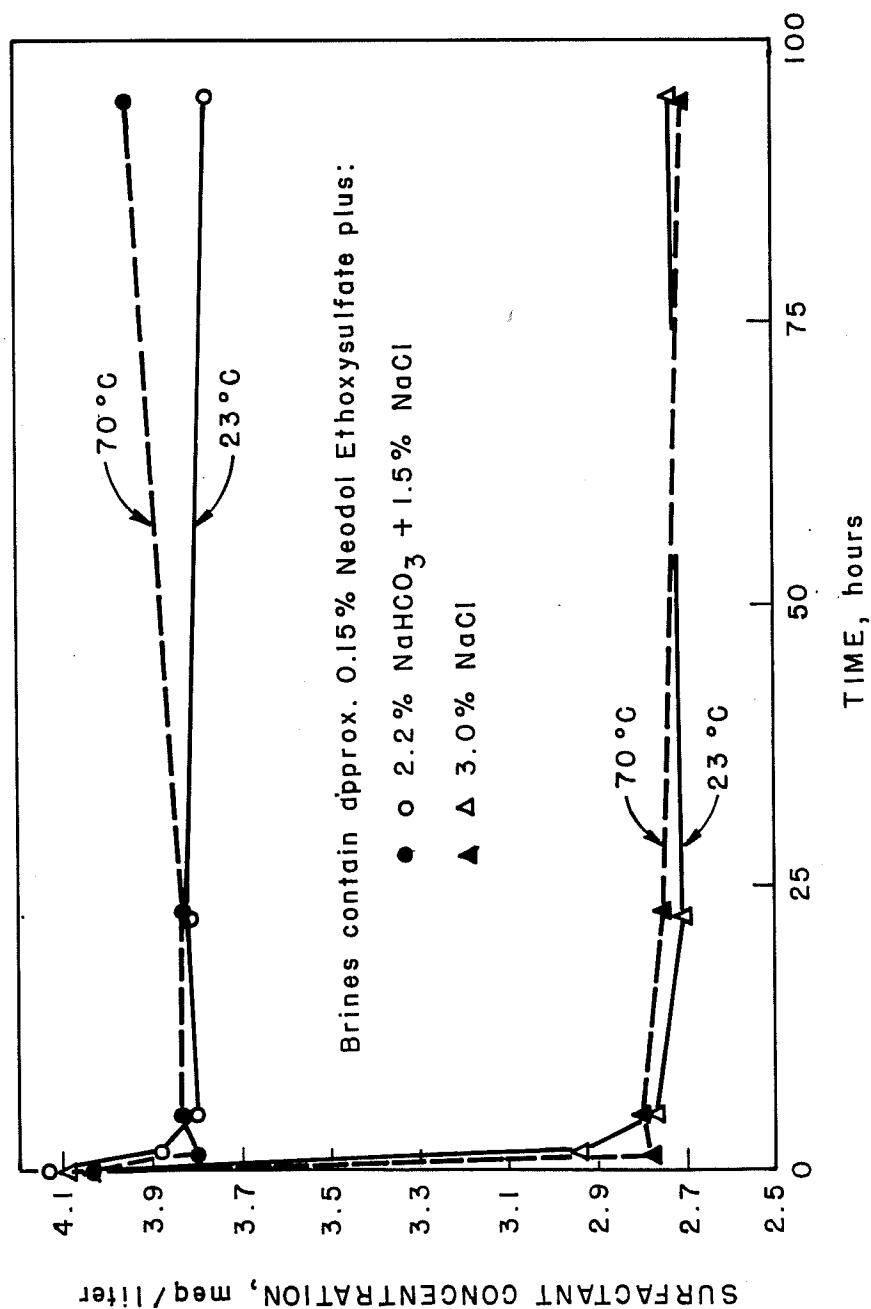


FIGURE 8. - Batch experiment designed to determine the adsorption of Neodol ethoxysulfate onto kaolinite in the presence of either Tronacarb plus sodium chloride (pH 8.9) or sodium chloride alone (pH 6.6). The supernatant surfactant concentration is shown versus time at two temperatures.

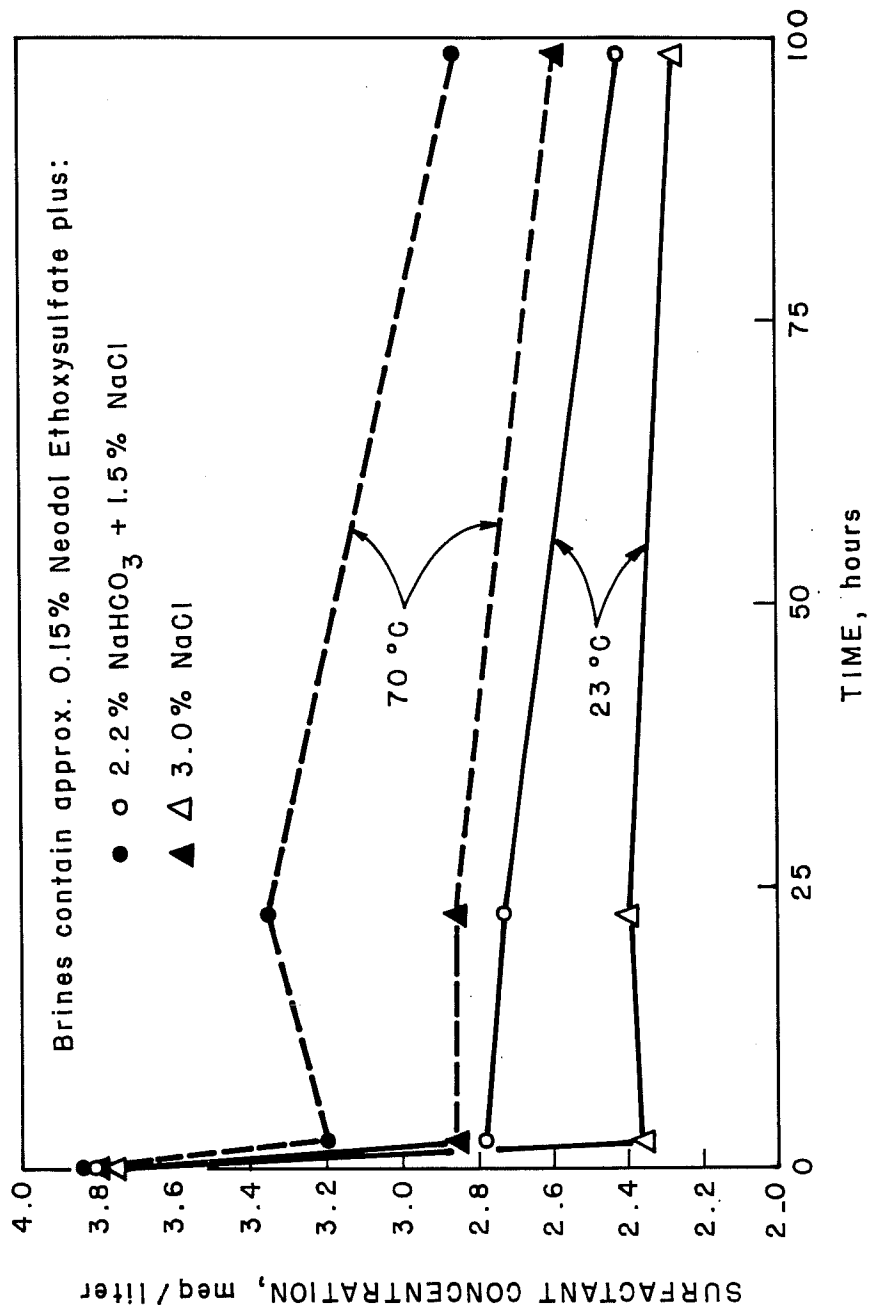


FIGURE 9. - Batch experiment designed to determine the adsorption of Neodol ethoxysulfate onto crushed Berea sandstone in the presence of either Tronacarb plus sodium chloride (pH 8.9) or sodium chloride alone (pH 6.6). The supernatant surfactant concentration is shown versus time at two temperatures.



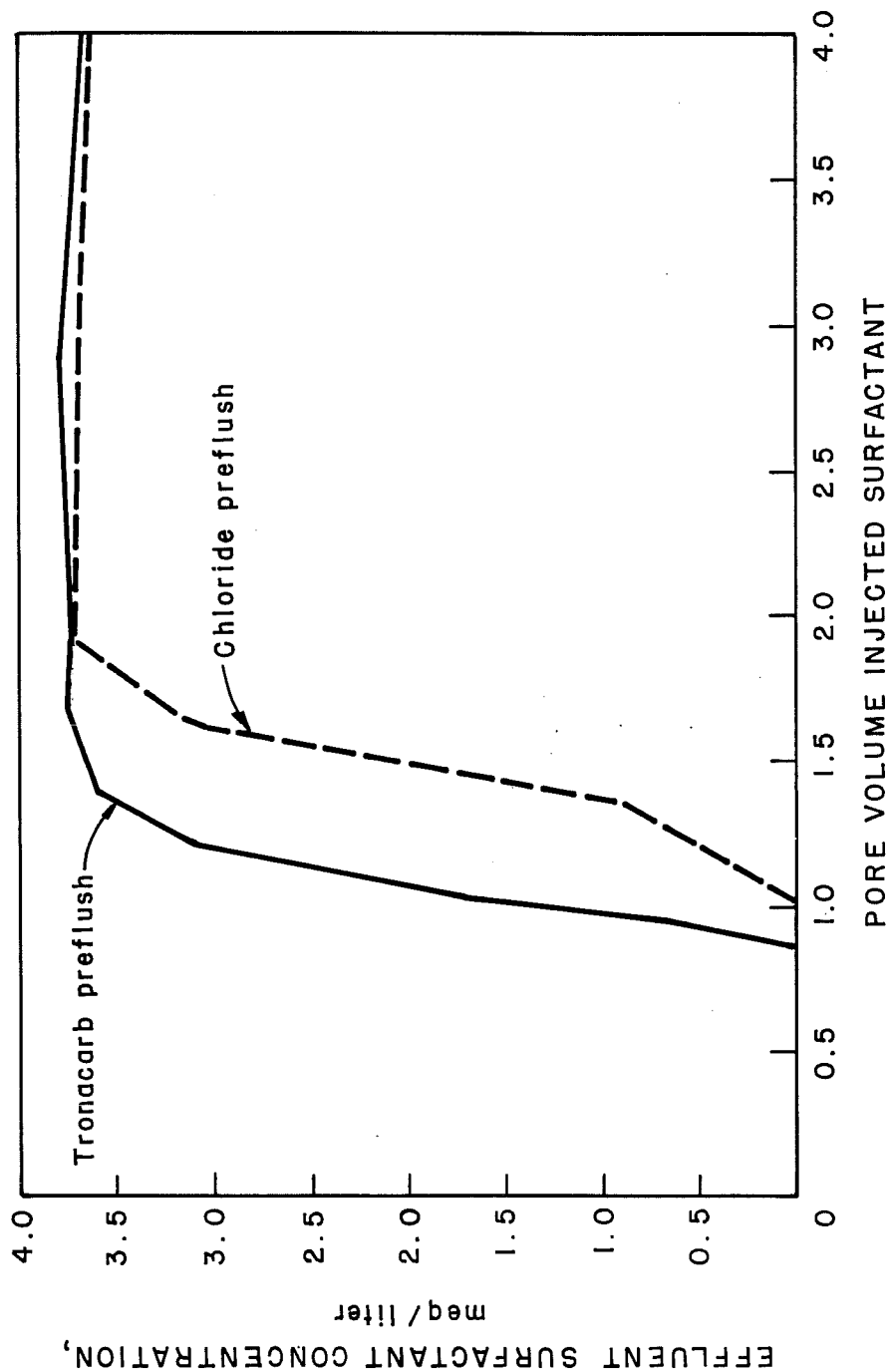
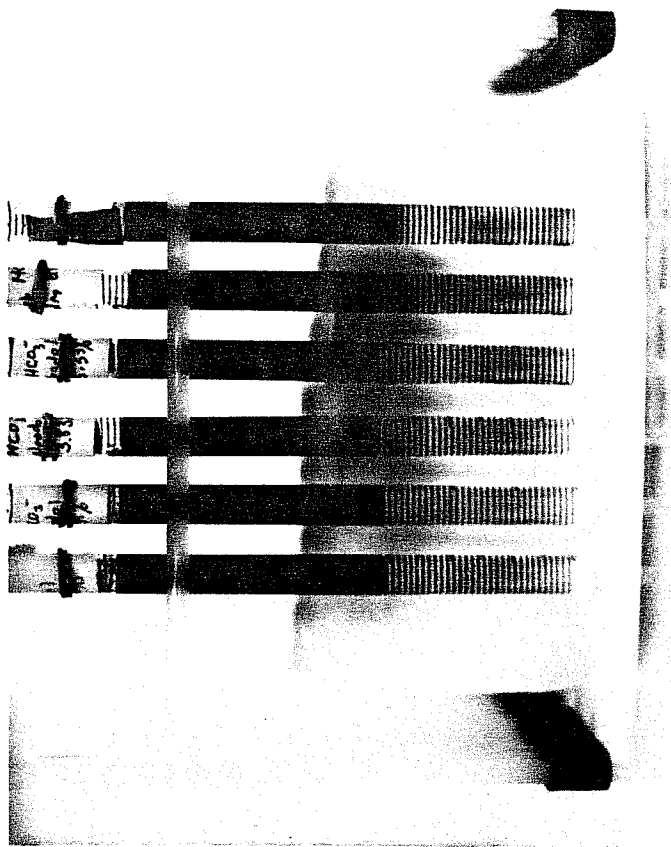


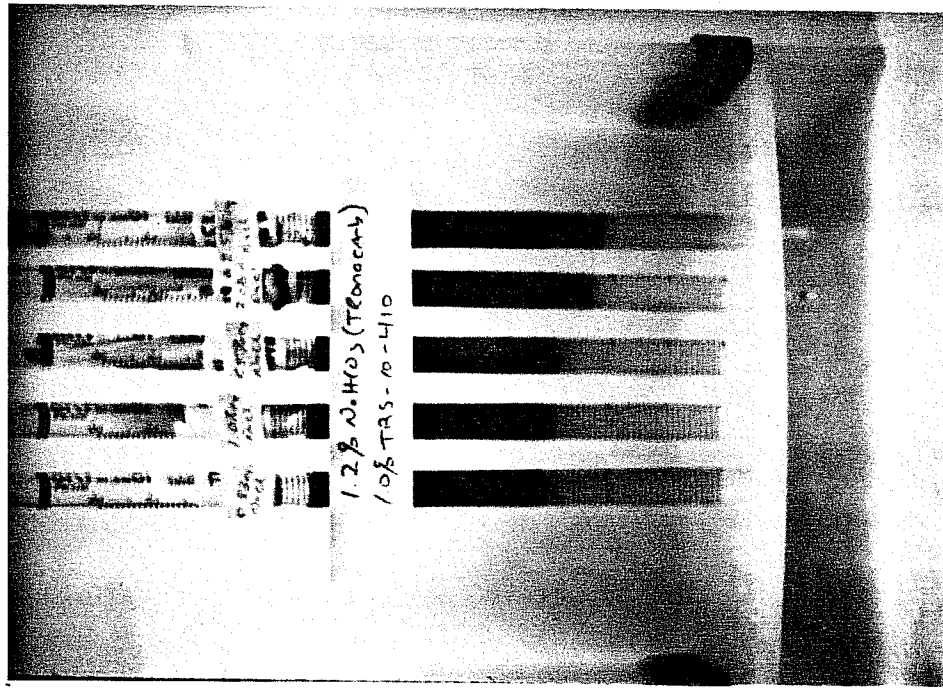
FIGURE 10. - The effectiveness of Tronacarb as a preflush is determined by monitoring the effluent concentration during surfactant injection into cylindrical 10-in. Berea sandstone cores. Breakthrough occurred earlier using a Tronacarb preflush indicating better protection against surfactant adsorption.

Aqueous solubility of petroleum soaps generated by contacting Wilmington crude oil with brines containing sodium bicarbonate (Tronacarb) and a synthetic anionic surfactant.



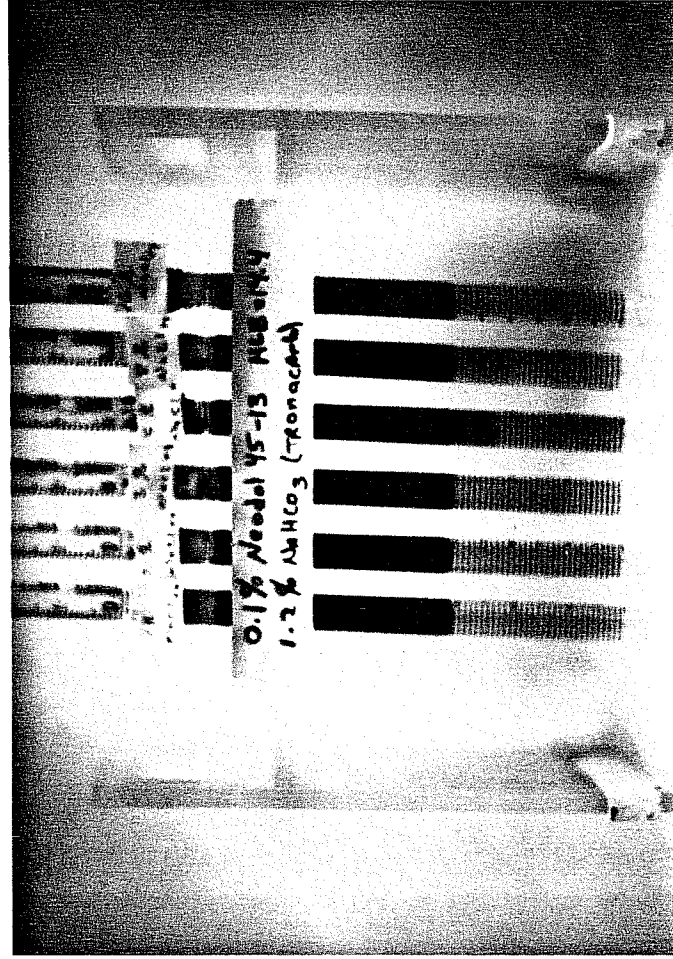
Photograph 1 - Photograph shows leaching of petroleum soaps into brines containing 1.2 percent sodium bicarbonate, 0.1 percent alcohol ethoxysulfate (Neodol 25-3S) and sodium chloride. Salinity increases left to right. Equivalent sodium chloride concentrations: 1.7, 2.4, 4.7, 6.2, 7.7, and 13.7 percent based on sodium content. Oil and brines were in contact for 12 hours at 73° C, WOR = 1.

Aqueous solubility of petroleum soaps generated by contacting Wilmington crude oil with brines containing sodium bicarbonate (Tronacarb) and a synthetic anionic surfactant.



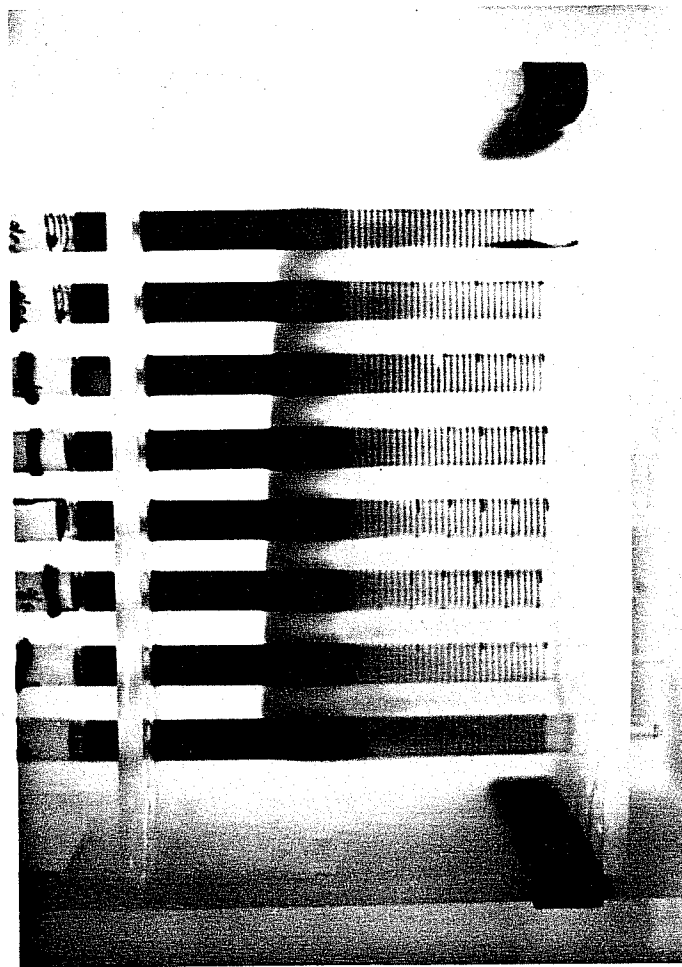
Photograph 2 - Photograph shows leaching of petroleum soaps into brines containing 1.2 percent sodium bicarbonate, 1.0 percent petroleum sulfonate (TRS-10-410) and sodium chloride. Salinity increases left to right: 0.8, 1.0, 1.5, 2.0, and 2.5 percent based on sodium content. Oil and brines were in contact for 12 hours at 45° C, WOR = 1.

Aqueous solubility of petroleum soaps generated by contacting Wilmington crude oil with brines containing sodium bicarbonate (Tronacarb) and a synthetic nonionic surfactant.



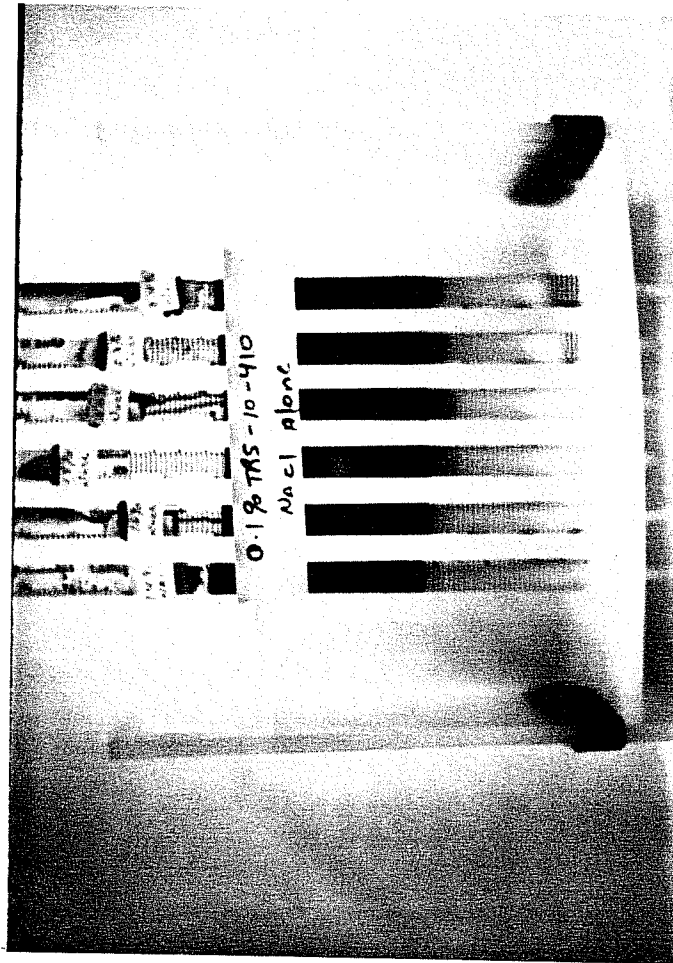
Photograph 3 - Photograph shows leaching of petroleum soaps into brines containing 1.2 percent sodium bicarbonate, 0.1 percent alcohol ethoxylate (Neodol 45-13), and sodium chloride. Salinity increases left to right. Equivalent sodium chloride concentrations: 1.0, 2.0, 3.0, 5.0, 8.0, and 16.0 percent based on sodium content. Oil and brines were in contact for 12 hours at 73° C, WOR = 1.

Aqueous solubility of the natural petroleum soaps contained in Wilmington crude oil in contact with brines containing a synthetic anionic surfactant.



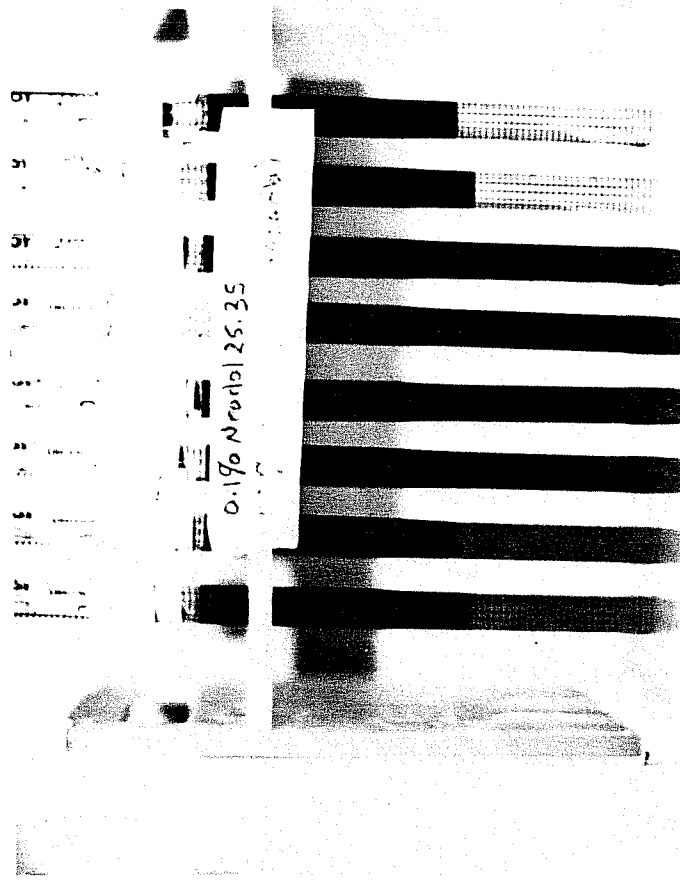
Photograph 4 - Photograph shows leaching of petroleum soaps into brines containing 0.1 percent alcohol ethoxysulfate (Neodol 25-3S) alone with sodium chloride. Salinity increases left to right: 0.8, 1.6, 3.8, 5.3, 6.8, 10.8, 12.8, and 15.8 percent sodium chloride. Oil and brines were in contact 12 hours at 73° C, WOR = 1.

Aqueous solubility of the natural petroleum soaps contained in Wilmington crude oil in contact with brines containing a synthetic anionic surfactant.



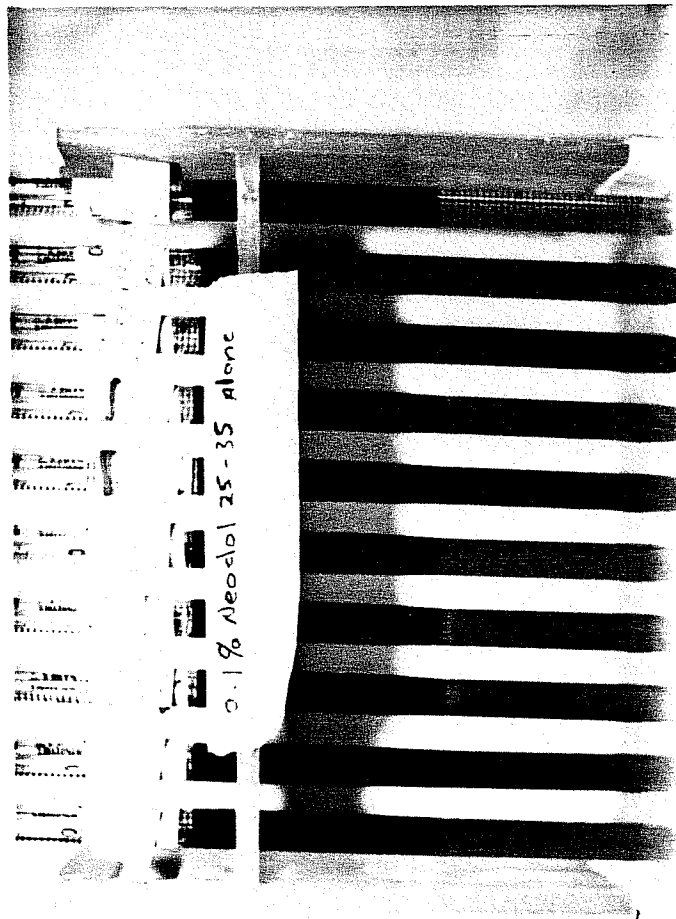
Photograph 5 - Photograph shows leaching of petroleum soaps into brines containing 1.0 percent petroleum sulfonate (TRS-10-410) alone with sodium chloride. Salinity increases left to right: 1.4, 1.6, 1.8, 2.0, 2.2, 2.4 percent sodium chloride. Oil and brines were in contact 12 hours at 45° C, WOR = 1.

Phase behavior of Wilmington crude oil and brines containing 0.1 percent anionic alcohol ethoxysulfate (Neodol 25-3S) and 1.2 percent sodium bicarbonate (Tronacarb) at various salinities.



Photograph 6 - Photograph shows lower phase emulsification at 73° C 10 days after creaming. Salinity increases left to right. Equivalent sodium chloride concentrations: 1.7, 2.4, 4.7, 6.2, 7.7, 9.7, 11.7, and 13.7 percent based on sodium content. WOR = 1.

Phase behavior of Wilmington crude oil and brines containing 0.1 percent anionic alcohol ethoxysulfate (Neodol 25-3S) alone at various salinities.



Photograph 7 - Photograph shows lower phase emulsification at 73° C 10 days after creaming. Salinity increases left to right: 0.8, 1.6, 3.8, 5.3, 6.8, 10.8, 12.8, 15.8, 17.8, and 20 percent sodium chloride. WOR = 1.

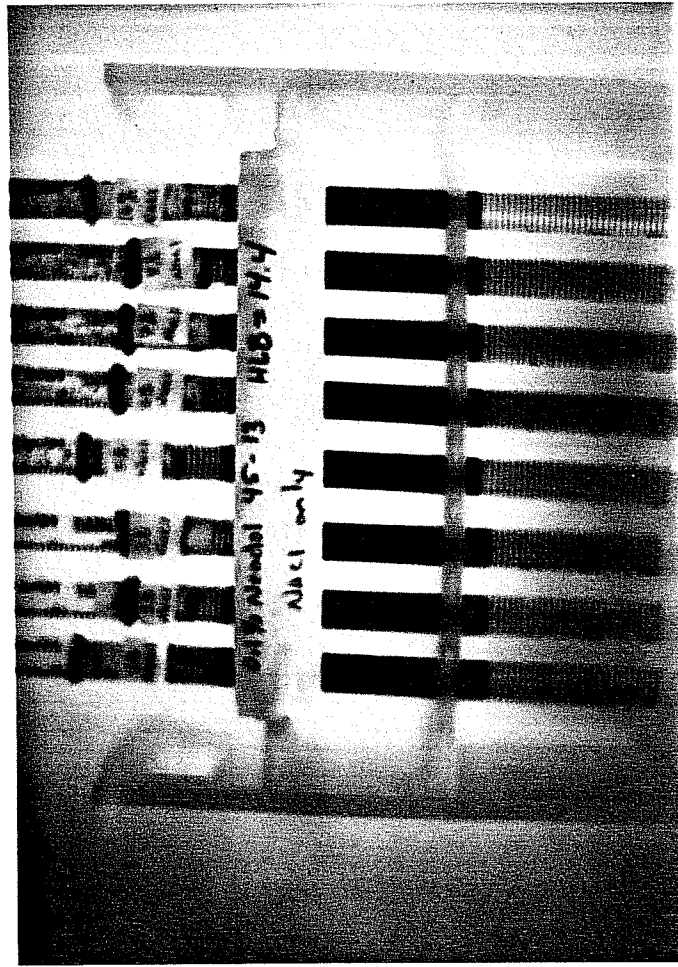


Phase behavior of Wilmington crude oil and brines containing 0.1 percent nonionic alcohol ethoxylate (Neodol 45-13) and 1.2 percent sodium bicarbonate (Tronacarb) at various salinities.



Photograph 8 - Photograph shows lower phase emulsification at 73° C 10 days after creaming. Salinity increases left to right. Equivalent sodium chloride concentrations: 1.0, 2.0, 3.0, 5.0, 6.0, 7.0, and 16.0 percent based on sodium content. Optimal salinity is approximately  $5 \pm 1$  percent, WOR = 1.

Phase behavior of Wilmington crude oil and brines containing 0.1 percent nonionic alcohol ethoxylate (Neodol 45-13) alone at various salinities.



Photograph 9 - Photograph shows no apparent lower phase emulsification at 73° C 10 days after creaming. Salinity increases left to right: 1.0, 2.0, 3.0, 5.0, 6.0, 7.0, 8.0, and 16.0 percent sodium chloride. No optimal salinity was identified by phase behavior, WOR = 1.